

OPEN AIR SURFACE CURE OF ELASTOMERS

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] Benefit of Provisional Application 60/438,548 filed January 6, 2003 is claimed

BACKGROUND OF THE INVENTION

[0002] This invention relates to curing methods for elastomers and to the compositions and articles prepared by such methods.

[0003] Elastomers can be vulcanized in a number of ways, for example with sulfur compounds or with organic peroxides. Sulfur vulcanization has the advantage of not being inhibited by oxygen at the surface of the article being molded, whereas organic peroxide cure methods have been limited to closed pressure molding (such as compression, transfer, and injection molding) because it is generally understood in the art that oxygen contacting the surface during molding reacts with the peroxy catalyst to cause hydroperoxy radicals which inhibit vulcanization and cause degradation of the resultant polymer. This results in tacky and/or partially cured elastomer surfaces. This is due to radicals in the polymer chain coupling with free oxygen to create hydroperoxy radicals. This hydroperoxy radical inhibits vulcanization and ultimately leads to degradation of the polymer. This phenomenon normally limits the production of peroxide-cured elastomers to molded goods. The three main types of molding are compression, transfer, and injection molding processes. All of these molding methods rely on an enclosed cavity for curing, and pressure to keep oxygen out of the system.

[0004] Typical cure mechanisms associated with sulfur vulcanization of elastomers are not normally inhibited by the presence of oxygen. This allows such sulfur cured elastomers to be cured in a wide variety of open surface methods in addition to the closed compression, transfer, and injection molding methods. Such open surface methods by which sulfur curing but not peroxide curing were practical in the prior art include: Open Hot Air Environment; Open Steam Environment; Open Salt Bath; and Open Sand Bath.

[0005] Although it is theoretically possible to peroxide-cure elastomers in an open-air environment by removing the oxygen from the curing environment by purging with nitrogen or another suitable material, such a method is unrealistic in commercial elastomer production since the curing environment is too large and would require an uneconomical supply of nitrogen to purge the cure area.

SUMMARY

[0006] It has been discovered that an organic peroxide-initiated elastomer composition comprising a metal carboxylate can be molded under open surface conditions to produce a tack free or low tack surface molding. The invention comprises the method of molding, the molding composition, the molding produced by the process, and molded articles prepared by the process.

DETAILED DESCRIPTION

[0007] Elastomers to which the invention is applicable are any which can be molded under open surface conditions using organic peroxide initiators. Examples of such elastomers include ethylene-propylene diene rubber (EPDM), nitrile rubber (NBR), polychloroprene (CR), hydrogenated NBR (HNBR), styrene-butadiene rubber (SBR), polybutadiene rubber (BR), ethylene-propylene copolymer (EPM), fluoroelastomers (FKM), silicone rubber (MQ, VMQ), acrylic rubber (ACM), Acrylonitrile-butadiene-styrene (ABS), polyethylene (PE), chlorosulfonated polyethylene (CSM), chlorinated polyethylene (CM) (also known as CPE), natural polyisoprene (NR), synthetic polyisoprene (IR), and ethylene-vinyl acetate (EVA). EPDM is the most typical elastomer presently used in this art.

[0008] Suitable organic peroxides are any of the ones which are used in the art of curing the elastomers. Examples include dicumyl peroxide, di-(t-butylperoxy)-diisopropylbenzene, 2, 5 dimethyl-2,5 - di-(t-butyl-peroxy) hexane (DBPH), 2,5-dimethyl-2,5-Di-(t-butyl-peroxy)hexyne-3 (Varox 130 type), n-Butyl 4,4-Di(t-butylperoxy) valerate (Varox 230 type), and 1,1 bis-(t-butylperoxy)-3,3,5-trimethyl-cyclohexane (Varox 231 type).

[0009] The amounts of peroxide are also any of the amounts used in the art of peroxide-cured molding elastomers, usually about 0.1 to 10 per cent, based on elastomer.

[0010] The composition can also include any cross-linking coagent. Some examples include trimethylol propane trimethacrylate (TMPTM), trimethylol propane triacrylate, triallyl cyanurate, bis maleimide, 1,2-vinyl polybutadiene; and the like.

[0011] The metal carboxylate is added by any means. Some examples include combining the carboxylate with the elastomer by conventional blending or pre-dissolving in a cross-linking coagent (typically in a concentration of about 5 to 25% by weight), and then adding the solution to the elastomer, for example in a ratio of about 2 to 20 parts by weight of the solution per 100 parts by weight of the elastomer.

[0012] Typical amounts of metal carboxylate compound are 0.1 to 10 parts by weight per hundred overall elastomer, peroxide, and metal carboxylate composition. Preferably 0.2 to 2.5 parts by weight of the metal carboxylate is used.

[0013] The metal compound can be any metal carboxylate, preferably C₂ to C₂₀ fatty acid, for example metal neodecanoate, metal propionate, metal naphtheneate, and/or metal octoate.

[0014] Suitable metals include, for example, cobalt, zirconium, manganese, zinc, iron, aluminum, and tin. Cobalt is the most preferred metal, and cobalt neodecanoate is the most preferred metal carboxylate. Mixtures of metal carboxylates are also suitable.

[0015] The curing conditions are any of those used in open surface molding of elastomers, for example open hot air, open steam, open salt bath, and open sand bath methods. While the novel compositions of the invention can be used in any molding method, the advantage of low tack to tack-free surfaces is an improvement most particularly applicable to open molding methods.

[0016] While not intending to be limited to any theory of operation, it is believed that incorporation of the metal compound in the peroxide-initiated elastomer formulation prevents oxygen from degrading the peroxy radicals on the elastomer surface.

EXAMPLES

[0017] In the following examples, all parts and percentages are by weight, unless otherwise indicated.

Example 1 (Comparative)

[0018] A formulation consisting of 100 parts EPDM elastomer (Dupont-Dow IP 4640 brand) was blended with 7.5 parts Dicumyl peroxide (Hercules DiCup 40 KE brand) and 5 parts Trimethylolpropane trimethacrylate (Sartomer SR 350 brand). The composition was mixed and molded under open air cure conditions at 330° F for 40 minutes and press cured for 45 minutes at 330° F. The following properties were measured: degree of tack on cured plaques, tensile strength, elongation, and modulus. The results are reported in the table below.

Examples 2 and 3 (Invention)

[0019] Example 1 was repeated except using 0.25 parts cobalt neodecanoate in Ex. 2 and 0.5 parts in Ex. 3, with the results reported in the table below.

[0020] As can be seen from the results of the comparative testing, the moldings of the invention had no tack on their surfaces whereas the molding of the comparative example had a tacky surface.

TABLE

<u>EXAMPLE</u>	<u>1</u>	<u>2</u>	<u>3</u>
Formulation			
EPDM ¹	100	100	100
Dicumyl peroxide ²	7.5	7.5	7.5
Trimethylolpropane trimethacrylate ³	5	4.75	4.5
Cobalt Neodecanoate		0.25	0.5
Mixing			
Cure Meter; ASTM D2084			
ODR, 320° F			
MH, in-lb	97.6	103.6	107.3
ML, in-lb	11.6	11.7	11.8
MH - ML, in-lb	86	91.9	95.5
Tc90, min	33.7	34.3	33.2
Ts2, min	1.25	1.27	1.26
Degree of flash tack	tacky	no tack	no tack
Plaques molded but not cured in carver press for 5 minutes @ 212° F			
Open Air Cure @ 330° F (min)			
Degree of tack on cured plaque	tacky	no tack	no tack

¹ Dupont-Dow IP4640 brand

² DiCup 40 KE brand

³ SR 350 brand (Sartomer Company)

Press Cure @ 330° F (min)	45	45	45
Physicals (Ambient conditions)			
Tension; ASTM D412			
Tensile Strength, lbf/in ²	285	330	330
Elongation, %	100	115	115
Modulus (100%), lbf/in ²	285	300	300

[0021] While the invention has been described and exemplified in sufficient detail to enable those skilled in the art to make and use it, other embodiments, alternatives, and modifications should become readily apparent without departing from the spirit and scope of the invention.